An Efficient Low Cost Prototype Air Sampler for Monitoring of Airborne Benzene and Toluene

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ABSTRACT

Air concentrations of benzene and toluene were monitored by home-made prototype air sampler for indoor and outdoor environments. The monitored areas consisted of chemistry and biological laboratory rooms at Nakhonsawan Rajabhat University, the traffic hot spot and university gate in winter season of January, 2017. For indoor source, the mean concentrations of benzene and toluene ranged from 0.05-28 $\mu gm^{-2}h^{-1}$ and 1.01-17 $\mu gm^{-2}h^{-1}$, respectively, while the concentrations of those compounds were higher at the traffic hot spot where the exhaust emission of vehicles was stringently regulated on a roadside (benzene 6.64-48.43 $\mu gm^{-2}h^{-1}$). The net results of the overall recovery were between 68%-85%. For indoor source, chemicals and air pollution caused by other compounds from household cleaning products or painting supplies did not have major effects on the uptake rate. On the other hand, transportation was the main cause of benzene for outdoor sampling site, however, toluene was not detected since it was able to enter the soil and water near waste disposal sites. Also, it is possible for toluene to be broken down in subsurface water, primarily by anaerobic microorganisms. Analysis was evaluated using gas chromatography coupled flame ionization detection (GC-FID). In conclusion, the results confirmed the home-made prototype air sampler have considerable potential utility for the short and long term indicative measurement of benzene and toluene with its simplicity of usage for both indoor and outdoor environments.

Keywords*: air sampler, benzene, toluene, prototype*

INTRODUCTION

Air pollution affects environment and causes a range of adverse human health which is why European Union (EU) and The World Health Organization (WHO) has set legal restrictions to limit the pollution concentration. Emerging volatile contaminants can be broadly defined as any naturally or synthetic chemicals such as particulate matter, volatile organic compounds (VOCs) and pesticides. Among air pollutants, benzene is considered a good representative of traffic emission from gasoline combustion and evaporation. Apart from benzene, toluene is considered to be one of the most toxic elements in the air as it often presents in paints, lacquer and glue as a cleaning and dying agent. It is also a constituent of gasoline and other

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aviation fuels. Hence, both benzene and toluene are classified as carcinogenic air pollutants, which can cause adverse health effects (Thammakhet et al., 2004).

Nakhonsawan is a province of Thailand which is a gateway to the northern region of the country. Currently, the city municipalities is facing traffic congestion, one of the biggest problems, especially during the annual festival such as New Year break and Songkran holiday, due to increase in uses of transport networks. Traffic emission in Nakhonsawan city is responsible for an extremely high level of ambient benzene released from vehicles and it is also proportional to population density. Moreover, benzene emission levels have been increased in the ambient air due to normal usage as a laboratory reagent, as well as a product of incomplete combustion of gasoline and diesel fuel. Hence, those two sampling sites, both of indoor and outdoor, were considered as hot spots with respect to air quality in the Nakhonsawan Rajabhat University and nearby.

There are two methods used for monitoring trace air pollutants. The active air sampling method employs an air pump to pull air through the sorbent while passive air sampling one monitors diffusion of gases over the sorbent (Murena 2007). Detailed descriptions of the indicative air measurement have been reported for either active or passive air sampling. Strandberg et al (2005) reviewed passive air sampling methods with thermal desorption for monitoring of 1,3-butadiene and benzene. This method with SKC-ultra and Radiello used as adsorbents has a high potential utility for personal monitoring both general and specific workplaces. However, it is generated by specially designed pump and the air flow rate was controlled by computer-controlled mass flow meter, making the sampler require power but noisy and higher cost. Passive air sampler is simple, and can be applied with a great number of sorbents, such as activated charcoal and porous polymers. The functional group of the sorbent indicates efficiency of the adsorption process for each pollutant. The main disadvantage is that this method requires long sampling period, while the efficiency is lost along the solvent desorption process.

There is still a need to design and develop the cost-effective, and efficient sampling technique with ease of use. The advantage of active air sampler is due to fast operation, however, it is costly and requires a specific component of device, while the passive air sampler employs the sorbent with diffusion but takes a long exposure time. In this sorbent enrichment aspect, combination of active and passive processes is a good alternative way and a challenge method for analysis of toxic air pollutants. It is possibly a compatible detector for wide range air pollutants with a high surface volume of sorbent. Meanwhile, this approach can be used only by a light weight battery and coupled to chamber containing a specific sorbent that matches the selected gas. Thus, the combination of active and passive air sampler meets the need of inexpensiveness, rapidness and easy to use under indoor-outdoor operation conditions.

The main objective of the present study is to design and develop a low cost hybrid air sampler using the tube packed with graphitized carbon blacks Carbopack X (CaX) sorbent for diffusion of passive device and the active air pump to incorporate the sampling rate. This work builds upon investigation of gas monitoring with a verity parameters including the amount of sorbents, types of extraction reagent and extraction time prior to analysis by using gas chromatography (GC).

METHODOLOGY

Hybrid air sampler construction

The main feature of the prototype air sampler is a lightweight sealed rechargeable battery (NS12-7.5, 12V7.5AH/24hr, 1.5 kg) powered fan muffler that minimizes the construction and operational factors to the users (Fig 1). The prototype air sampler consists of a glass tubes (15 mm. id. x 60 mm length) filled with CaX sorbent and covered with cotton on the top to avoid spilling. Sampling filters are placed inside the chamber connected to the free-solvent box with timer-controlled fans which produce a constant airflow through the sorbent materials. In order to avoid any re-entry gas to the free-solvent box, the PTFE pipe connected between the chamber and the box was designed. The pipe connector was cleaned after use to prevent contamination. The total size of the device was 70x30 cm with the weight by 250 g.

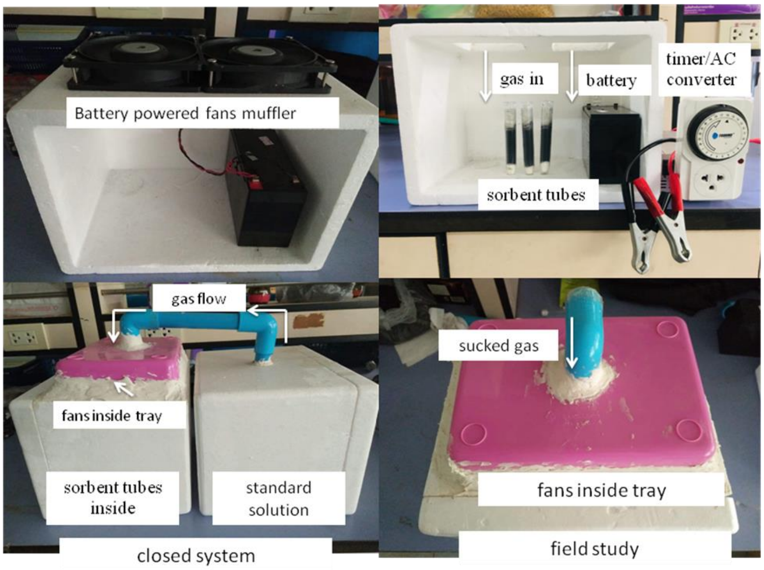

Figure 1. The home-made prototype air sampler

Preliminary experiments

The operation started from 20 mgL^{-1} standard benzene and toluene in a close system. Standard compounds were sucked in by sampling pump and further blown through the CaX sorbent filter. After sampling, CaX sorbents were removed from the glass tube and transferred to cap vial acetone solution. Extraction was performed with utrasonicator and stored at -4^{o}C prior GC-FID analysis for an acceptable recovery.

To obtain the optimum conditions of the hybrid system, the CaX sorbent of 3, 4, 5, 6 and 7 g was filled into a glass tube. In addition, the exposure time indicated as 1, 2, 3, 4, 5, 6, 12, 18 and 24 hr was investigated while the volume of acetone was examined at 5, 10 and 15 mL using ultrasonicator. Finally, the desorption times of 3, 5, 7 and 9 min were explored for optimal effective recovery. To evaluate the optimum conditions, the selected parameter was analyzed while other parameters were kept constant. Five replicates were made for all treatments before a field study.

GC investigation

Gas analysis was investigated using GC (Agilent) with a DB-1fused-silica mega-bore analytical column (15 m × 0.53 mm i.d., 1.5 μm thickness) with FID detector. Separation and detection were performed by injection 1 μL of extracted solution in the split/splitless mode. Pure nitrogen gas (99.99% purity) was used as a carrier at the flow rate of 1.2 mLmin^{-1} with the temperature of injection port, column oven and detector of 60, 120 and 170ºC, respectively.

Field experiments

Upon the preliminary experiments, prototype air sampler experiment with the appropriate conditions was carried out under environmental conditions. The device was placed in the Chemistry and Biological laboratory rooms at the Faculty of Science and Technology, Nakhonsawan Rajabhat University, Thailand as an indoor protocol. For an outdoor experiment, the same appropriate design was placed on the busy road at the traffic light intersection in Nakhonsawan city, Thailand and at Nakhonsawan Rajabhat University's gate. In order to protect the device from air velocity and rain, the device was mounted inside a 500x400x200 mm stainless-steel which served as a shelter while maintaining the proper air sampling. Sampling was carried out in January, 2017 for a week of 24 hr.

RESULTS AND DISCUSSION

Influence of the amount of CaX sorbent

The prototype air sampler containing 3, 4, 5, 6 or 7 g efficiently adsorbed benzene and toluene. However, recovery higher than 80% was found in the 5 g CaX treatment. This indicated that a glass tube half filled with sorbents caused an increase in uptake rate. Conversely, high amount of CaX might increase the effective path length and decrease the uptake rate. Besides, the 3 and 4 g CaX treatments were lack of efficiency, somewhat due to a decrease in active surface area to adsorb benzene and toluene (Fig 2).

Comparison of two target volatile compounds revealed small differences in uptake rates. This, once again, suggested that CaX sorbent appeared to be an efficient adsorbent for benzene and toluene.

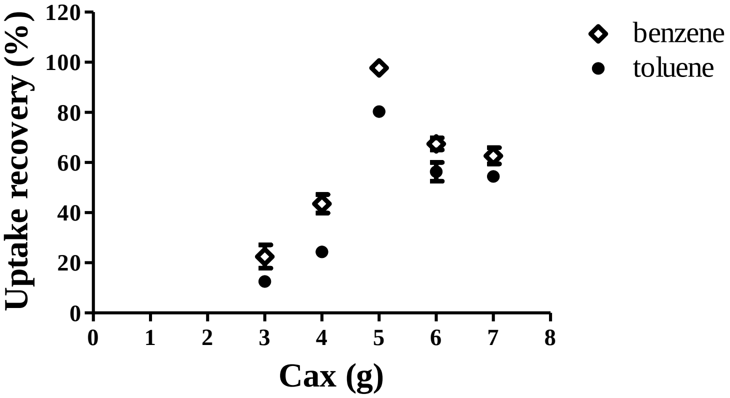

Figure 2. Percentage recovery of uptake rate for benzene and toluene standards in relation to the amounts of CaX sorbent

Influence of exposure time

Considering the exposure times of 1, 2, 3, 4, 5, 6, 12, 18 and 24 hr, it was found that 1-6 hr and 12 hr suggested a linear response relationship with recoveries of 77.4-106.6% for benzene while for toluene, it was found at the exposure time of 1-6 hr with the recoveries of 72.5-85.6% as shown in Fig 3. A non-linear behavior could be described in term of mass transfer that limited gas diffusion rate within the boundary layer (Polulhet et al., 2015). Consequently, the reverse diffusion process would be considered and involved in developing a suitable parameter of specific home-made device.

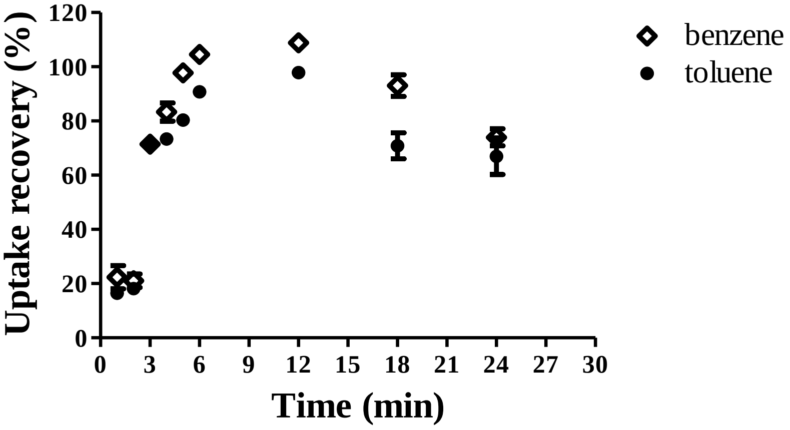

Figure 3. Percentage recovery of uptake rate for benzene and toluene standards in relation to time exposure

Influence of extraction volumes

The removal of volatile compounds was necessary in order to determine the effect of extraction solution volume. From Fig 4, the recovery of extracted volume using 10 mL acetone was consistent for both volatile compounds at up to 80%, while those of 5 and 15 mL acetone under the same conditions dropped down at the range of 64-67%. Caution should be advised due to volatilization of acetone during the extraction process which could become a problem for determination of benzene and toluene uptake. Thus, the recoveries of both benzene and toluene reported herein were only valid on the selected timescale at 7 min for each replicate.

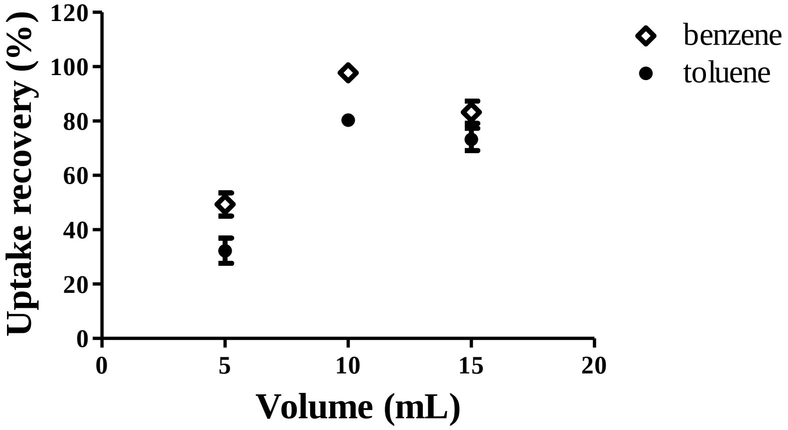

Figure 4. Percentage recovery of uptake rate for benzene and toluene standards in relation to extraction volume

Influence of extraction time

As shown in Fig. 5, the influence of extraction time on benzene and toluene uptake rates was assessed at the time varied between 3-9 min. In case of benzene, the corresponding loss was 26% within 7 min extraction time, while the other showed over 50% analyte loss. There was a slight decrease in toluene recovery due to the loss of acetone.

In conclusion, preliminary studies indicated that the optimum condition for benzene and toluene uptake rate by using home-made hybrid air sampler should be 5 g CaX with 10 mL acetone for 7 min extraction time. It was recommended that at least 12 and 4 hr were required as the maximum exposure time for benzene and toluene uptake, respectively.

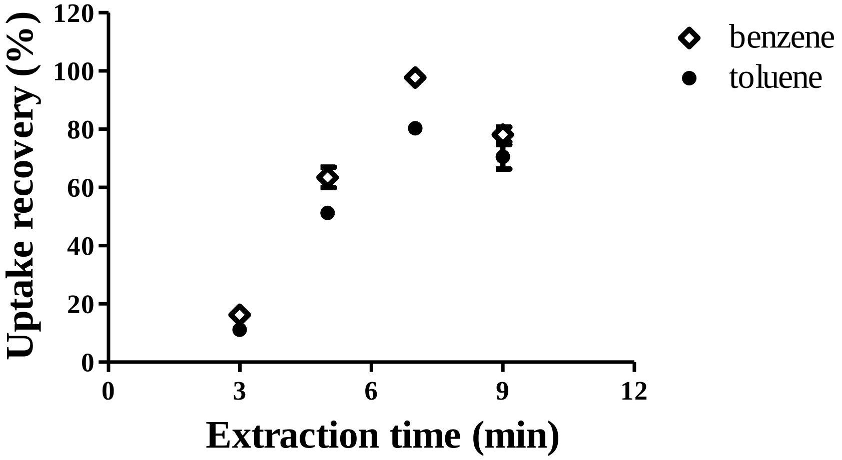

Figure 5. Percentage recovery of uptake rate for benzene and toluene standards in relation to the extraction time

GC-FID analysis

The main retention times for benzene and toluene were 1.6 and 2.8 min, respectively. The linearity was observed in the range of 70 pg-450 ng for both compounds. The limit of detection for benzene and toluene were 5 and 8 ng, respectively.

Field studies

As mentioned in section 2.4, 6 the selected studied sites included Science building (1st floor^{t}-4th floor), intersections and university gate. These studied led to the development of an easy-to-used device to monitor benzene and toluene produced from indoor and outdoor sources. The emission rates from 1st floor and 2nd floor were relatively low for indoor investigation, with the value of benzene and toluene ranging from 0.05-1.52 $\mu gm^{-2}h^{-1}$ to 1.01-1.55 $\mu gm^{-2}h^{-1}$, respectively. Measured emission rates at 3rd floor for benzene and toluene exhibited the highest value of 21-28 $\mu gm^{-2}h^{-1}$ and 16-17 $\mu gm^{-2}h^{-1}$, respectively. More than 50% of the total emission was contributed by a variety of chemicals in laboratory rooms while both buildings and furnishing materials generated volatile substances emission. In laboratory rooms, benzene and toluene were emitted mostly from reactions and chemicals which created numerous pollutants, evenly conducted in the fume hood.

Emission rates of benzene and toluene in the range of 4-10 $\mu gm^{-2}h^{-1}$ and 4-4.5 $\mu gm^{-2}h^{-1}$ were also observed from 4th floor and it could be generated from biological laboratory rooms and building materials. The concentration of benzene (42.45 - 55.02 $\mu gm^{-2}h^{-1}$) and toluene (12.95-31.68 $\mu gm^{-2}h^{-1}$) at the intersection, allowing identifying transportation as the main emitter. At the university gate, only benzene emission was detected in the range of 36.53-55.18 $\mu gm^{-2}h^{-1}$.

Variation in levels of benzene and toluene could occur due to wind velocity, temperature, humidity and seasonal changes such as monsoon air masses during the short sampling period. However, information of benzene and toluene level would be evidence on facing risks of toxic pollutants. Additionally, concentrations of both compounds varied due to spatial variation within the shortened sampling period, resulting in their significant loss after 2 weeks of storage.

CONCLUSIONS

The home-made and low cost prototype air sampler could be used to monitor benzene and toluene emission generated from either indoor or outdoor sources of volatile compounds. Such high recoveries of extraction imply that the entire pore with low volume pores was related to the adsorption process. Results presented that indoor benzene and toluene were emitted in the range of 0.05-21 $\mu gm^{-2}h^{-1}$and 1.01-27 $\mu gm^{-2}h^{-1}$, respectively. The emission from outdoor intersections and university gate was found to be 36.53-55.18 $\mu gm^{-2}h^{-1}$ and 12.95-31.68 $\mu gm^{-2}h^{-1}$, respectively. The results of the study indicated that the laboratory room was the dominant source of benzene and toluene, while exhaust emission of motorbikes, cars, buses and vans were also the main pollution sources of outdoor benzene. Hence, prototype air sampler can serve as an alternative approach to apply for various air pollutants across several sampling sites. Portable prototype air sampler can be designed to meet the benefits of our goals, such as simple for operating with low noise, less energy consuming, economy with high recovery of validation method. In future work, wind velocity and flow rate should be studied and used as a supplementary data as these parameters during different seasons cause potential effects on the sampling rate.

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